



UNIVERSITÀ
DEGLI STUDI
FIRENZE

FLORE

Repository istituzionale dell'Università degli Studi di Firenze

Pulse Electron Spin Resonance and Quasi - Elastic Light Scattering of Winsor Microemulsions

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

Original Citation:

Pulse Electron Spin Resonance and Quasi - Elastic Light Scattering of Winsor Microemulsions / P.Baglioni; C.M.C.Gambi; D.Goldfarb. - STAMPA. - 84:(1991), pp. 133-138.

Availability:

This version is available at: 2158/347739 since:

Terms of use:

Open Access

La pubblicazione è resa disponibile sotto le norme e i termini della licenza di deposito, secondo quanto stabilito dalla Policy per l'accesso aperto dell'Università degli Studi di Firenze (<https://www.sba.unifi.it/upload/policy-oa-2016-1.pdf>)

Publisher copyright claim:

(Article begins on next page)

Pulse electron spin resonance and quasi-elastic light scattering of Winsor microemulsions

P. Baglioni*), C. M. C. Gambi**), and D. Goldfarb***)

*) Department of Chemistry, University of Udine, Udine, Italy

**) Department of Physics, University of Florence, Florence, Italy

***) Isotopes Department, The Weizmann Institute of Science, Rehovot, Israel

Abstract: The interfacial region of Winsor microemulsions has been studied at the molecular level by electron spin echo modulation technique using doxyl stearic acid spin probes. We found that the water and oil molecules are located at opposite sides of the interface, and that the alcohol molecules are mainly located at the water side of the interface for all the microemulsions studied. Thus, alcohol, oil, and water molecules belong to well separated regions of the interface. No significant variation of the water and alcohol molecules distribution at the interface is observed in Winsor I and III microemulsions as a function of salt addition. The oil molecules, however, penetrate deeper into the interfacial film in Winsor I as compared to Winsor III microemulsions. The inner part of the interface of Winsor I and II microemulsions changes as a function of salt addition, whereas the outer part remains unchanged; in Winsor III microemulsions both the inner and the outer parts of the interface remain unchanged. This behavior is in agreement with the asymmetry in the interfacial properties expected for well-defined aggregates (w/o and o/w) and with the symmetry of the bicontinuous microemulsions interfacial film. Quasi-elastic light-scattering has been used to compare the structure of the Winsor microemulsions with and without probe addition and components deuteration.

Key words: Microemulsion; interfacial film; electron spin echo resonance; quasi-elastic light-scattering; nitroxide probe

Introduction

Electron spin echo spectroscopy is a pulse version of electron spin resonance (ESR) and it enables the detection of very weak magnetic interactions [1] between the unpaired electron of a suitable molecular paramagnetic probe and nearby nuclear spins, which usually cannot be probed by conventional ESR spectroscopy. This technique allows to study the interfacial region of dispersed systems at the molecular level. In recent years dispersed systems such as micellar solutions [2], microemulsions [3], and vesicles [4] have been successfully studied by this technique. In the present paper, we used this technique to study at the molecular level the interfacial region of Winsor microemulsions [5, 6] which separates oil and water. Winsor microemulsions in-

clude oily aggregates dispersed in water or aqueous aggregates dispersed in oil or bicontinuous structures (i.e., oily and aqueous interconnecting channels), thus showing a large class of interesting phase behaviors. It is expected that the interfacial regions of microemulsions would show compositions and structures related to the microemulsions macroscopic structure.

In this work (and in [7]) the interfaces of Winsor microemulsions have been studied by electron spin-echo modulation technique (ESEM). This technique gives a description of the interface in terms of water and oil penetration and distribution of the alcohol molecules at the interface. The role of the salt and that of the interfacial alcohol are also elucidated. Doxyl stearic acids, with the doxyl group along the alkyl chain in the 5 position, or 10, or 16, respec-

tively, were used as paramagnetic probes and three series of the Winsor microemulsions with deuterated water, oil, or alcohol molecules were studied. The magnetic dipole-dipole interactions between the unpaired electron of the doxyl group and deuterium nuclei were detected by ESEM technique. It should be noted that the probe addition, as well as the component deuteration may, in principle, perturb the system. The use of a probe is necessary in electron spin resonance and in fluorescence studies, whereas deuteration is used, for example, in neutron scattering and nuclear magnetic resonance studies. Therefore, a structural investigation of the system should be done to elucidate the effect of the probe addition [8] and of the components' deuteration. A preliminary quasi-elastic light-scattering (QELS) investigation of the structural change due to components deuteration is also presented.

Experimental

Materials

Toluene, 1-butanol, sodium dodecyl sulfate (SDS) and sodium chloride were Merck Germany products. The water was from a Millipore Milli-Q system. Doxyl stearic acids with the doxyl group in 5, 10 or 16 position of the alkyl chain (x-DSA) were from Molecular Probes, Eugene, Oregon, USA. Deuterated 1-butanol- d_{10} and toluene- d_8 (purity $\geq 99\%$) were from Aldrich USA, D_2O was from Carlo Erba (Italy) (purity $\geq 99\%$). All the products were used without further purification.

A-system

A mixture of brine (46.8%), toluene (47.25%), SDS (1.99%), and 1-butanol (3.96%) was prepared for different salinities (NaCl/brine) in the range 3–10%. All the proportions are given in w/w. The phase equilibria sequence Winsor I, III, II is observed when the brine salinity is increased from 3% to 10%. Winsor I (3–5.3% salinity) is a microemulsion of oil-in-water aggregates coexisting with an oily phase; Winsor II (7.5–10%) is a microemulsion of water-in-oil aggregates coexisting with an aqueous phase, and Winsor III (5.4–7.4%) consists of a bicontinuous microemulsion coexisting with both oily and aqueous phases. The composition of all the phases, the microemulsion structure, and the interfaces between microemulsion and excess phase are well known [9–23].

The samples were stabilized at $T = 22^\circ\text{C} \pm 0.1^\circ\text{C}$ in a bath for more than 1 week; after attaining equilibrium, the phases were separated and placed in the same bath. Afterwards no further phase separation was observed. Stabilization and phase separation were identical for A,

B, and C systems. A stock solution of 5-DSA probe was prepared in chloroform. Films of the probe generated in the sample tube by evaporating the chloroform were dissolved in the microemulsion. The tube was sealed to prevent evaporation, then gently mixed and equilibrated at $T = 22^\circ\text{C}$ for at least 24 h before the measurement.

B-system

Three series of the Winsor microemulsions set were prepared with deuterated water, alcohol or oil. The alcohol/surfactant and oil/surfactant mole ratios were 7.73 and 74.21, respectively, for all the samples. The salinity S_M (salt/brine mole ratio) was changed from 0.943×10^{-2} to 3.31×10^{-2} ; the brine/surfactant molar ratio was in the range 368–351, depending on the salinity. These molar ratios correspond to the composition by weight reported above for the non-deuterated samples.

C-system

A given amount of the deuterated microemulsion was divided into three parts and each x-DSA probe was added to each part following the procedure described for the A-system. The probe concentration was 1×10^{-4} M, about 1/1000 the SDS concentration in the microemulsion [12, 24].

Electron spin-echo modulation (ESEM) technique

For theoretical and experimental details on the ESEM techniques see [1, 25]. The ESEM measurements were performed on the samples of the C-system.

Quasi-elastic light-scattering

The apparatus used, the experimental procedure followed, and data analysis are described in [26]. The light-scattering measurements were performed on the samples of system A and B.

Results and discussion

ESEM measurements

An echo-decay envelope has been measured for all the microemulsions studied. The normalized deuterium modulation depth (NDMD) is the experimental parameter which gives the information on the probe location and on the alcohol, oil, and water distributions at the microemulsion interface [27]. In order to interpret the ESEM results, we

have to recall that x-DSA probes are weakly water soluble and comicellize with the surfactant molecules [28, 29]. The carboxyl group is located at the polar micellar surface and the alkyl chain inside the micelle. Furthermore, it is known for micellar solutions that the doxyl group in the 5 position along the stearic acid chain is close to the SDS polar head group at the 2nd–3rd methylene [30–32]. When the probe presents an extended conformation (typical of reverse micelles [4], [33]) increasing x moves the doxyl group further away from the surface of the micelle deeper into the oil phase. Therefore, if the water molecules are deuterated a decrease in the NDMD vs x is expected, whereas an increase is expected when oil molecules are deuterated. In case of a folded conformation (typical of direct micelles [4, 31, 32]) a decrease of the NDMD from $x = 5$ to 10 and an increase from $x = 10$ to 16 for deuterated water molecules indicates that the probe bends close to $x = 10$; the reverse is obtained for deuterated oil molecules.

Figure 1 shows the NDMD or Winsor I microemulsions as a function of the doxyl position for the different deuterated components. The NDMD is quite large for deuterated oil molecules

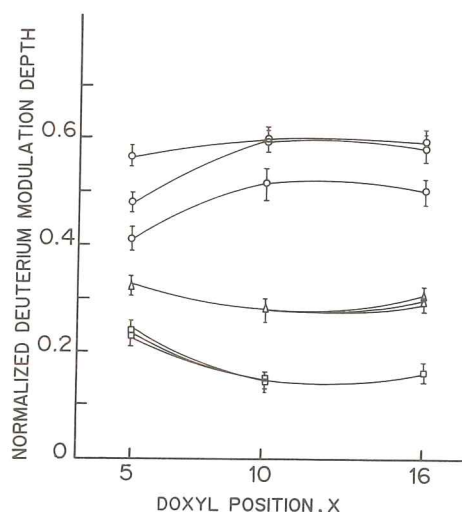


Fig. 1. Normalized deuterium modulation depth vs doxyl group position for Winsor-I microemulsions. The square, triangle, and circle symbols correspond to values obtained deuterating water or alcohol or oil, respectively. Each set of curves corresponds to the microemulsions with $S_M = 0.94 \times 10^{-2}$; 1.27×10^{-2} and 1.59×10^{-2} , respectively. For the salt addition the normalized deuterium modulation depth increases if oil is deuterated and is practically constant if alcohol or water are deuterated. The salinity values correspond approximately to 3, 4, and 5% w/w

(toluene- d_8) and decreases for deuterated alcohol and water molecules. For the last two components the NDMD values are identical, within the experimental errors, throughout the whole salinity range. This indicates that both the probe location at the microemulsion interface and the probe conformation do not vary with salt addition to the system. The trends of the NDMD curves of the deuterated alcohol or water molecules are similar and opposite to that of the deuterated oil molecules. These trends are consistent with a folded conformation of the probe, which in turn is compatible with the structure of the system (oil in water aggregates). Once the probe location and conformation is known the following description of the interface can be given. The probes see alcohol and water molecules on the water side and toluene on the oil side. These regions are well separated and the addition of salt does not change the probe location and conformation, but it increases the oil penetration at the interface, as shown by the increase of the NDMD with increasing salinity. Quantitative results obtained by comparison of the Winsor I microemulsions with the SDS/NaCl/water/1-butanol micellar solutions [7] indicate that oil penetrates up to the 4–5th methylene from the surfactant polar head group.

The NDMD of Winsor II microemulsions is found to increase linearly with the doxyl position when toluene molecules are deuterated, as shown in Fig. 2. The opposite trend is observed when alcohol or water molecules are deuterated, but the linearity is maintained only for deuterated alcohol. The curves' trends of the deuterated oil and alcohol molecules indicate an extended probe conformation and support the assignment of the oil and alcohol to locations at opposite sides of the interface. As the salinity increases a shift of the curves is observed which can be interpreted as due to an increase of the amount of the interfacial oil and to a decrease of the amount of interfacial alcohol. However, we cannot exclude the possibility that the probe itself moves towards the oil side. The NDMD for the 5-DSA probe in the microemulsion with deuterated water molecules is not affected by salt addition, while a decrease is observed for the other doxyl group positions. This behavior is consistent with the trend reported above for deuterated oil and alcohol molecules, leading to similar conclusions. In this system the trend of the NDMD as a function of the doxyl group position for deuterated water molecules is not linear. In our opinion, no physical insight can be drawn from this trend since the

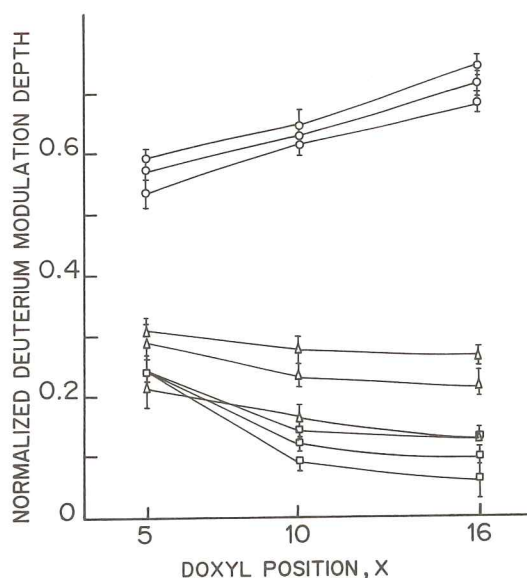


Fig. 2. Normalized deuterium modulation depth vs doxyl group position for Winsor-II microemulsions. The symbols have the same meaning as in Fig. 1. Each set of curves corresponds to the microemulsions with $S_M = 2.61 \times 10^{-2}$; 2.95×10^{-2} and 3.31×10^{-2} , respectively. For the salinity addition the normalized deuterium modulation depth increases if oil is deuterated, and decreases if alcohol and water are deuterated. The salinity values correspond approximatively to 8, 9, and 10% w/w

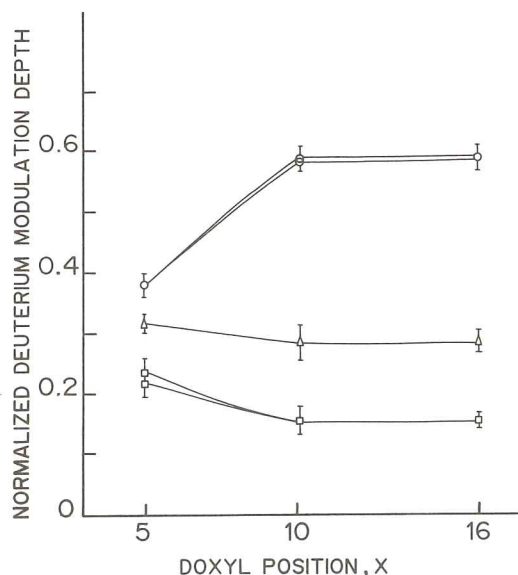


Fig. 3. Normalized deuterium modulation depth vs doxyl group position for Winsor-III microemulsions. The symbols have the same meaning as in Fig. 1. Each set of curves corresponds to the Winsor-III microemulsions with $S_M = 1.93 \times 10^{-2}$ and 2.09×10^{-2} . For the salinity addition the normalized deuterium modulation depth decreases slowly if oil is deuterated and increases slowly if water is deuterated: no variation is observed for deuterated alcohol. The salinity values correspond approximatively to 6 and 6.5% w/w

NDMD values for some curves are very weak (in particular for 16-DSA is close to zero) and are subject to large experimental errors that could have been underestimated.

The NDMD profiles of Winsor-III microemulsions are shown in Fig. 3. The profiles for deuterated alcohol and water molecules are very similar to those of Winsor-I microemulsions, indicating that the probe experiences the same environment on the water side of the interface, whereas for deuterated toluene the NDMD at $x = 5$ is lower than that of Winsor-I microemulsions (the other values remaining similar). Quantitative analysis [7] indicates that toluene penetrates the interface only up to the 8–9th methylene from the surfactant polar head group. As for Winsor-I and -II microemulsions, the different profiles for deuterated toluene, alcohol, and water molecules are in good agreement with the conclusion that these components occupy well-separated regions in the microemulsions. It is also found that the interfacial film of these bicontinuous microemulsions is little affected by the salinity variation.

QELS Analysis

5-DSA spin-labeled microemulsions and unlabeled microemulsions have been studied under the same experimental conditions in order to investigate possible perturbations induced by the probe on the microemulsion structure. A probe concentration $\leq 3 \times 10^{-4}$ M does not change the average mutual diffusion coefficient (\bar{D}) for all the microemulsions studied, indicating that the probe concentration of the ESEM measurements (1×10^{-4}) does not perturb the microemulsion structure [8]. In this paper, preliminary QELS results on Winsor-I and -II microemulsions with deuterated components are reported. The experimental \bar{D} values and the polydispersity factors are given in Table 1. For comparison, the non-deuterated microemulsions have also been studied under identical experimental conditions. In principle, physical constants (viscosity of the continuous medium and volume fraction of the dispersed phase) and/or structural parameters (hydrodynamic radius and

Table 1. Average mutual diffusion coefficient and polydispersity factor of Winsor-I and -II microemulsions for nondeuterated and deuterated components

S_M ($\times 10^2$)	\bar{D} [cm^2/s] ($\times 10^7$)	μ_2/\bar{I}^2 (%)	Win- sor	S (%)	
0.94	3.09	11	I	3	
0.94	3.05	13	I	—	toluene- d_8
0.94	3.05	10	I	—	1-butanol- d_{10}
0.94	2.08	10	I	—	D_2O
3.31	3.31	7	II	10	
3.31	2.95	5	II	—	toluene- d_8
3.31	3.12	9	II	—	1-butanol- d_{10}
3.31	3.62	10	II	—	D_2O

diffusion virial coefficient) affect the \bar{D} value [24]. As the viscosity of deuterated water is about 23% higher than that of normal water [34] the observed 50% difference between the \bar{D} values of deuterated water and deuterated alcohol or oil of the Winsor I microemulsion cannot be due only to a viscosity change. Furthermore, we expect that the volume fraction of the dispersed phase, for the same Winsor-I microemulsion, should be similar to that of the non-deuterated microemulsion. Thus, it seems likely that the structural parameters, or only one of them, change when water is deuterated. We obtained different \bar{D} values for the Winsor-II microemulsions with water, oil, or alcohol molecules deuterated. To distinguish between the effect of the structural parameters and that of the physical constants, composition analysis, viscosity measurements, and structural investigation of the diluted samples are in progress in our laboratory.

Conclusion

The ESEM analysis enables the following description of the interfacial region of a Winsor microemulsions set. For all the microemulsions studied the interfacial water, alcohol, and oil molecules belong to well-separated regions. The interfacial alcohol molecules are mainly located on the water side, whereas the interfacial water and oil molecules are at opposite sides of the interface. Upon salt addition, the water side changes little for Winsor-I and

-III microemulsions, and for Winsor-II microemulsions at the lower salinity range. Oil molecules penetrate up to the 4–5th methylene from the surfactant polar head group in Winsor-I microemulsions, and up to the 8–9th methylene in Winsor-III microemulsions. This indicates a variation in the SDS alkyl chain packing and/or conformation which takes place upon the Winsor-I to Winsor-III phase transition. The oil side in Winsor-I microemulsions and the water side in Winsor-II microemulsions show, respectively, the highest variation vs the salt addition; in both cases they correspond to the inner part of the interface; the outer part of the interface remains unchanged. The asymmetry of the Winsor-I and -II interfacial regions is consistent with the existence of a strong spontaneous curvature which leads to oil-in-water or water-in-oil aggregates. The symmetry of the Winsor-III microemulsions' interfacial film, deduced by the invariance of the NDMD values as a function of salt addition, is compatible with the bicontinuous microemulsion structure (weak spontaneous curvature and flexible interfacial film) [35, 36].

The ESEM results are also in agreement with the x-ray and neutron-scattering analyses [17–20] that give an interfacial film thickness of about 10 Å. The oil penetration to the 4–5th or 8–9th methylene of the SDS chain, deduced by ESEM analysis implies a similar thickness.

Quasi-elastic light-scattering has been used to compare the structure of Winsor microemulsions with and without probe addition. It showed that the probe concentration of the ESEM measurements does not perturb the microemulsion structure. To study the effect of the components deuteration a QELS study is in progress. Preliminary results show different \bar{D} values upon deuteration of oil, water, or alcohol.

Acknowledgements

We sincerely thank J. M. Di Meglio, L. Léger, and C. Taupin for having encouraged this work and for very helpful discussions. Thanks are due to the Israel, Italy scientific exchange program sponsored by the Italian CNR and the Israeli Ministry of Science and Development which made the above collaboration possible. This study was made possible in part by funds granted to D.G. through a fellowship program sponsored by the Charles H. Revson Foundation.

References

1. Kevan L, Bowman MK (1990) In: Modern Pulsed and Continuous — Wave Electron Spin Resonance. New York, Wiley
2. Baglioni P, Kevan L (1987) *J Phys Chem* 91:1516
3. Maldonado R, Szajdzinska-Pietek E, Kevan L (1984) *Faraday Discuss Chem Soc* 78:165
4. Kevan L, Baglioni P (1990) *Pure Appl Chem* 62:275
5. Winsor PA (1948) *Trans Faraday Soc* 44:376
6. Winsor PA (1968) *Chem Rev* 68:1
7. Baglioni P, Gambi CMC, Goldfarb D (1991) *J Phys Chem* 95:2577
8. Baglioni P, Ferroni E, Gambi CMC (in preparation) *J Phys Chem*
9. Bellocq AM, Biais J, Clin B, Gelot A, Lalanne P, Lemanceau B (1980) *J Colloid Interface Sci* 74(2):311
10. Pouchelon A, Meunier J, Langevin D, Chatenay D, Cazabat AM (1980) *Chemical Physics Letters* 76(2):277
11. Pouchelon A, Chatenay D, Meunier J, Langevin D (1981) *J Colloid Interface Sci* 82(2):418
12. Pouchelon A (1982) thesis, Paris
13. Guéring P, Lindman B (1985) *Langmuir* 1:464
14. Cazabat AM, Langevin D (1981) *J Chem Phys* 74(6):3148
15. Cazabat AM, Chatenay D, Langevin D, Meunier J, Léger L (1984) In: Mittal KL, Lindman B (eds) *Surfactants in Solution*. Plenum, New York, vol 3, p 1729
16. Chatenay D, Urbach W, Cazabat AM, Langevin D (1985) *Phys Rev Lett* 54(20):2253
17. Auvray L, Cotton JP, Ober R, Taupin C (1984) *J Physique* 45:913
18. Auvray L, Cotton JP, Ober R, Taupin C (1984) *J Phys Chem* 88:4586
19. Auvray L, Cotton JP, Ober R, Taupin C (1986) *Physica* 136B:281
20. Auvray L (1985) thesis, Paris
21. Guest D, Auvray L, Langevin D (1985) *J Physique Lett* 46:1055
22. Lachaise J, Graciaa A, Martinez A, Rousset A (1981) *Thin Solid Films* 82:55
23. Langevin D, Guest D, Meunier J (1986) *J Colloids and Surfaces* 19:159
24. Cazabat AM, Langevin D, Meunier J, Pouchelon A (1982) *Adv Colloid Int Sci* 16:175
25. Goldfarb D, Fauth JM, Tor Y, Shanger A (1991) *J Am Chem Soc* 113:1941
26. Chittofrati A, Lenti D, Sanguineti A, Visca M, Gambi CMC, Senatra D, Zhou Z (1989) *Progr Colloid Polym Sci* 79:218
27. Kevan L (1988) In: Fox MA, Chanon M (eds) *Photoinduced Electron Transfer, Part B*. Elsevier, Amsterdam, pp 329—394
28. Ramachandran C, Pyter RA, Mukerjee P (1982) *J Phys Chem* 86:3198
29. Pyter RA, Ramachandran C, Mukerjee P (1982) *J Phys Chem* 86:3206
30. Baglioni P, Ottaviani MF, Martini G (1986) *J Phys Chem* 90:5878
31. Szajdzinska-Pietek E, Maldonado R, Kevan L, Jones RRM (1985) *J Am Chem Soc* 107:6467
32. Szajdzinska-Pietek E, Maldonado R, Kevan L, Jones RRM (1985) *J Am Chem Soc* 107:784
33. Baglioni P, Nakamura H, Kevan L (in press) *J Phys Chem*
34. Chang NJ, Kaler E (1985) *J Phys Chem* 89:2996
35. de Gennes PG, Taupin C (1982) *J Phys Chem* 86:2294
36. Mitchell DJ, Ninham BW (1981) *J Chem Soc Faraday Trans II* 77:601

Authors' address:

Cecilia M. C. Gambi
Department of Physics
L. E. Fermi 2
I-50142 Florence, Italy